

## 4. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

### 4.1 PRODUCTION

In 1825, Faraday isolated benzene from a liquid condensed by compressing oil gas. Benzene was first synthesized by Mitscherlich in 1833 by distilling benzoic acid with lime. Benzene was first commercially recovered from light oil derived from coal tar in 1849 and from petroleum in 1941 (IARC 1982a). Several years after the end of World War II, the rapidly expanding chemical industry created an increased demand for benzene that the coal carbonization industry could not fulfill. To meet this demand, benzene was produced by the petroleum and petrochemical industries by recovery from reformat and liquid by-products of the ethylene manufacturing process (Purcell 1978).

Currently, benzene is commercially recovered from both coal and petroleum sources. More than 98% of the benzene produced in the United States is derived from the petrochemical and petroleum refining industries (OSHA 1987b). These sources include refinery streams (catalytic reformats), pyrolysis gasoline, and toluene hydrodealkylation. Catalytic reformat is the major source of benzene (Greek 1990). Between 1978 and 1981, catalytic reformats accounted for approximately 44-50% of the total U.S. benzene production (Fishbein 1988a). During catalytic reforming, cycloparaffins (also known by the obsolescent term “naphthenes”) such as cyclohexane, methyl cyclohexane, and dimethylcyclohexane are converted to benzene by isomerization, dehydrogenation, and dealkylation, and paraffins in naphtha (such as hexane) are converted to benzene by cyclodehydrogenation. The process conditions and the catalyst determine which reaction will predominate. The benzene is recovered by solvent extraction (e.g., with sulfolane or tetraethylene glycol). Pyrolysis gasoline is a liquid by-product produced by the steam cracking of lower paraffins (gas oil) or heavier hydrocarbons (heavy naphtha). Pyrolysis gasoline contains unsaturated aliphatic hydrocarbons (such as ethylene and propylene) and aromatics. Several integrated pyrolysis gasoline treatment processes are available including partial hydrogenation and extractive distillation; hydrogenation, hydrodesulfurization, and solvent extraction; or partial hydrogenation, desulfurization, hydrocracking, hydrodealkylation, and distillation for the optimization of benzene yield and the recovery of benzene (IARC 1982a; Purcell 1978). In the toluene hydrodealkylation process, toluene or toluene/xylene mixtures are reacted with hydrogen at temperatures up to 730 °C and demethylated to produce benzene and methane. Another process whereby toluene is converted to benzene and xylenes by transalkylation or disproportionation is also used for the production of benzene (Purcell 1978). Small quantities of benzene are also

produced from destructive distillation of coal used for coke manufacture. Benzene is derived from the light oil fraction produced during the coking process (Greek 1990; Purcell 1978). New coking, gasification, and liquefaction processes for coal are all potential sources of benzene (IARC 1982a). Of the total U.S. production capacity of 17.2 billion pounds in 1993, catalytic reformats constituted 45%, toluene and xylene 29%, pyrolysis gasoline 23% and coke oven <3% (SRI 1993).

In 1994, benzene was the 17th highest volume chemical produced in the United States, compared to the 18th and 17th ranks in 1993 and 1992, respectively (C&EN 1994; Kirschner 1995; Reisch 1994). Based on actual and preliminary production data and excluding tar distillers and coke-oven operators, the U.S. production of benzene was 14.7 billion pounds in 1994, 12.3 billion pounds in 1993, 1.64 billion gallons (12.0 billion pounds) in 1992, and 1.57 billion gallons (11.5 billion pounds) in 1991 (C&EN 1995). Production data from 1984 to 1994 indicate that the production of benzene increased by about 4% annually (C&EN 1995). Preliminary production data reported for the first and second quarters of 1995 show potential towards continuing this trend: 3.8 billion L (7.4 billion pounds) were produced (USITC 1995).

SRI (1994) lists the following companies as producers of benzene in the United States in 1994: Amoco Oil Co., Texas City, Texas; Ashland Oil Co., Catlettsburg, Kentucky; BP Oil, Alliance, Louisiana, and Lima, Ohio; Chevron Chemical Co., Pascagoula, Mississippi, Philadelphia, Pennsylvania, and Port Arthur, Texas; CITGO Petroleum Corp., Corpus Christi, Texas, and Lake Charles, Louisiana; Coastal Eagle Point Oil Co., Westville, New Jersey; Coastal Refining and Marketing, Inc., Corpus Christi, Texas; Dow Chemical, USA, Freeport, Texas, and Plaquemine, Louisiana; Exxon Chemical Co., Baton Rouge, Louisiana, and Baytown, Texas; Fina Oil and Chemical Co., Port Arthur, Texas; Hess Oil Virgin Islands Corp., St. Croix, U.S. Virgin Islands; Huntsman Chemical Corp., Bayport, Texas; Koch Refining Co., Corpus Christi, Texas; Lyondell-CITGO Refining Co. Ltd., Houston, Texas; Lyondell Petrochemical Co., Channelview, Texas; Marathon Oil Co., Texas City, Texas; Mobil Oil Corp., Beaumont, Texas, and Chalmette, Louisiana; Occidental Petroleum Corp., Chocolate Bayou, Texas, and Corpus Christi, Texas; Phibro Energy USA, Inc., Houston, Texas; Phillips Petroleum Co., Sweeny, Texas; Phillips Puerto Rico Core Inc., Guayama, Puerto Rico; Quantum Chemical Co., La Porte, Texas; Shell Chemical Co., Deer Park, Texas, and Wood River, Illinois; Southwestern Refining Co., Inc., Corpus Christi, Texas; Sun Co., Inc., Marcus Hook, Pennsylvania and Toledo, Ohio; Texaco Chemical Co., El Dorado, Kansas; and the UNO-VEN Co., Lemont, Illinois. In addition, the United States International Trade Commission lists the following

companies as producers: Oxy Petrochemicals, Inc., Dallas, Texas, and Kalama Chemical, Inc., Seattle, Washington (USITC 1995). Facilities listed as being responsible for producing the top 50% of regional capacity in the United States include: Chevron Chemical (18%); Exxon Chemical Company (8%); Shell Chemical Company (7%); Dow Chemical Company (7%); BP Oil Company (7%); and Occidental Petroleum Corporation (7%) (SRI 1995).

According to the Toxics Release Inventory (TRI), 472 facilities in the United States produced or processed benzene in 1993 (TRI93 1995). Table 4-1 lists the facilities in each state that manufacture or process benzene, the intended use, and the range of maximum amounts of benzene that are stored on site. The TRI data listed in Table 4-1 should be used with caution since only certain types of facilities were required to report. Therefore, this is not an exhaustive list.

#### **4.2 IMPORT/EXPORT**

The import of benzene into the United States is dependent on domestic production and demand. Imports of benzene (both petroleum and coal tar derived) into the United States were approximately 200 million L (387 million pounds) in 1990, 305 million L (591 million pounds) in 1991, 272 million L (528 million pounds) in 1992, 376 million L (729 million pounds) in 1993, and 304 million L (589 million pounds) in 1993 (USDOD 1995). The largest exporters of benzene to the United States during 1991-93 were Canada, Brazil, the Netherlands, and Mexico (USDOD 1994). As in the case of import, the export of benzene from the United States to other countries is dependent on domestic and world production and demand. The 1990-94 data indicate a decline in export volumes for benzene during this period. Exports of benzene (both petroleum and coal-tar derived) to other countries were approximately 289 million L (560 million pounds) in 1990, 54 million L (105 million pounds) in 1991, 63 million L (123 million pounds) in 1992, 3.3 million L (6.4 million pounds) in 1993, and 59.6 million L (115 million pounds) in 1994 (USDOD 1995). The largest importers of benzene from the United States are Canada, the Netherlands, Taiwan, and South Korea (USDOD 1994).

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**Table 4-1. Facilities That Manufacture or Process Benzene**

State <sup>a</sup>	Number of facilities	Range of maximum amounts on site in thousands of pounds <sup>b</sup>	Activities and uses <sup>c</sup>
AK	4	0-10000	1, 3, 4, 8, 10
AL	18	0-50000	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 13
AR	4	1-10000	1, 3, 4, 7, 13
AZ	2	10-1000	1, 6, 10, 13
CA	35	0-50000	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 13
CO	2	1000-10000	1, 3, 4, 6, 7
DE	4	1-50000	1, 6, 7, 9, 12, 13
GA	6	0-10000	1, 2, 4, 8, 9, 10, 11
HI	2	1000-10000	1, 2, 6
IA	1	1000-10000	1, 4
IL	26	1-100000	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13
IN	18	1-100000	1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 13
KS	10	0-50000	1, 3, 4, 5, 6, 7, 8, 9, 10, 13
KY	12	1-50000	1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 13
LA	40	0-500000	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 13
MD	3	1-10000	7, 8, 9
MI	28	0-10000	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 13
MN	3	1-100000	1, 3, 4, 6, 8, 9
MO	7	0-100	8, 9, 13
MS	6	10-50000	1, 3, 4, 6, 7, 8
MT	4	100-500000	1, 2, 3, 4, 6, 7, 8, 9
NC	3	0-1000	1, 5, 11
ND	1	10000-50000	1, 2, 3, 4, 7
NE	1	0-1	11
NJ	12	1-50000	1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 13
NM	4	1-10000	1, 3, 4, 6, 8, 13
NY	5	1-1000	1, 2, 4, 5, 9, 11, 13
OH	25	0-100000	1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 13
OK	6	1-50000	1, 2, 3, 4, 5, 6, 7, 8, 9, 13
OR	1	1000-10000	10
PA	21	0-50000	1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 13
PR	5	100-50000	1, 2, 3, 5, 6, 7, 8
SC	3	0-1000	1, 5, 7, 12
TN	9	0-10000	1, 3, 5, 6, 7, 8, 9, 12, 13
TX	94	0-500000	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13
UT	8	10-50000	1, 2, 3, 4, 6, 7, 8, 9, 10, 13
VA	5	1-1000	1, 2, 3, 5, 6, 7, 9, 11
VI	1	100000-500000	1, 2, 3, 4, 7

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**Table 4-1. Facilities That Manufacture or Process Benzene (continued)**

State <sup>a</sup>	Number of facilities	Range of maximum amounts on site in thousands of pounds <sup>b</sup>	Activities and uses <sup>c</sup>
WA	6	100-100000	1, 2, 3, 4, 6, 7, 8
WI	4	1-10000	1, 6, 9, 12, 13
WV	8	1-10000	1, 4, 5, 6, 7, 8, 9, 13
WY	5	0-10000	1, 3, 4, 5, 6, 7, 8, 10

Source: TRI93 1995

<sup>a</sup> Post office state abbreviations used<sup>b</sup> Data in TRI are maximum amounts on site at each facility<sup>c</sup> Activities/Uses:

- |                               |                                  |
|-------------------------------|----------------------------------|
| 1. Produce                    | 8. As a formulation component    |
| 2. Import                     | 9. As a product component        |
| 3. For on-site use/processing | 10. For repackaging only         |
| 4. For sale/distribution      | 11. As a chemical processing aid |
| 5. As a by-product            | 12. As a manufacturing aid       |
| 6. As an impurity             | 13. Ancillary or other uses      |
| 7. As a reactant              |                                  |

### 4.3 USE

Benzene has been used extensively as a solvent in the chemical and drug industries, as a starting material and intermediate in the synthesis of numerous chemicals, and as a gasoline additive (NTP 1994).

Benzene recovered from petroleum and coal sources is used primarily as an intermediate in the manufacture of other chemicals and end products. The major uses of benzene are in the production of ethylbenzene, cumene, and cyclohexane. Ethylbenzene (55% of benzene production volume) is an intermediate in the synthesis of styrene, which is used to make plastics and elastomers. Cumene (24%) is used to produce phenol and acetone. Phenols are used in the manufacture of phenolic resins and nylon intermediates; acetone is used as a solvent and in the manufacture of pharmaceuticals. Cyclohexane (12%) is used to make nylon resins. Other industrial chemicals manufactured from benzene include nitrobenzene (5%), which is used in the production of aniline, urethanes, linear alkylbenzene sulfonates, chlorobenzene, and maleic anhydride (Eveleth 1990; Greek 1990; HSDB 1996). Benzene is also a component of gasoline since it occurs naturally in crude oil and since it is a byproduct of oil refining processes (Brief et al. 1980; Holmberg and Lundberg 1985). Benzene is especially important for unleaded gasoline because of its anti-knock characteristics. For this reason, the concentration of aromatics, such as benzene, in unleaded fuels has increased (Brief et al. 1980). The percentage by volume of benzene in unleaded gasoline is approximately 1-2% (NESCAUM 1989).

The EPA has listed benzene as a hazardous air pollutant and a hazardous waste (EPA 1977, 1981~). In addition, there is sufficient evidence to support classifying benzene as a human carcinogen (Group A) (IRIS 1996). One result of EPA's action is that the widespread use of benzene as a solvent has decreased in recent years. Many products that used benzene as solvents in the past have replaced it with other organic solvents; however, benzene may still occur as a trace impurity in these products. Less than 2% of the amount produced is used as a solvent in such products as trade and industrial paints, rubber cements, adhesives, paint removers, artificial leather, and rubber goods. Benzene has also been used in the shoe manufacturing, and rotogravure printing industries (EPA 1978b; Farm Chemical Handbook 1993; OSHA 1977). In the past, certain consumer products (such as some paint strippers, carburetor cleaners, denatured alcohol, and rubber cement used in tire patch kits and arts and crafts supplies) contained small amounts of benzene (Young et al. 1978). Other consumer products

that contained benzene were certain types of carpet glue, textured carpet liquid detergent, and furniture wax (Wallace et al. 1987).

The Consumer Products Safety Commission (CPSC) withdrew an earlier proposal to ban consumer products, except gasoline and laboratory reagents, that contained benzene as an intentional ingredient or as a contaminant at 0.1% or greater by volume. The withdrawal of the rulemaking was based on CPSC findings that benzene was no longer used as an intentional ingredient and that the contaminant levels remaining in certain consumer products were unlikely to result in significant exposures (NTP 1994). Products containing more than 5% benzene, and paint solvents and thinners containing 10% or more of petroleum distillates such as benzene, are required to meet established labeling requirements. In a guidance document targeting school science laboratories, the CPSC recommended that benzene not be used or stored in schools. The document identified benzene as a carcinogen and ascertained that the hazards posed by its use in high school laboratories may be greater than its potential usefulness.

The use of benzene in certain pesticides has been canceled (HSDB 1996). Under the Federal Insecticide, Fungicide, Rodenticide Act (FIFRA), the EPA established a voluntary cancellation of registered products containing benzene as an active ingredient (HSDB 1996; IRIS 1996). Benzene was once used alone or in formulations to control screwworms on animals, and as an early fumigant for grain (HSDB 1996). The EPA also required labeling on pesticides containing benzene as an inert ingredient. The U.S. Food and Drug Administration (FDA) regulates benzene as an indirect food additive under the Food, Drug, and Cosmetics Act (FDCA). Under the FDCA benzene is restricted to use only as a component of adhesives used on articles intended for packaging, transport, or holding foods (FDA 1977a).

#### **4.4 DISPOSAL**

Benzene-containing wastes, such as commercial chemical products, manufacturing chemical intermediates, and spent solvents, are subject to federal and/or state hazardous waste regulations (HSDB 1996). Regulations governing the treatment and disposal of benzene-containing wastes are presented in Chapter 7. Waste by-products from benzene production processes include acid and alkali sludges, liquid-solid slurries, and solids (EPA 1982f; Saxton and Narkus-Kramer 1975). In the past, landfilling and lagooning have been the major methods of disposal of benzene-containing industrial

wastes (EPA 1982f). In addition to biodegradation, a portion of the benzene is expected to be lost due to volatilization. Unfortunately benzene, along with other hazardous contaminants, also leaches into groundwater from the lagooned wastes. Currently, the recommended method of disposal is to incinerate solvent mixtures and sludges at a temperature that ensures complete combustion. The recommended methods for combustion are liquid injection incineration at a temperature range of 650-1,600 °C and a residence time of 0.1-2 seconds; rotary kiln incineration at a temperature range of 825-1,600 °C and residence times of seconds for liquids and gases, and hours for solids; fluidized bed incineration at a temperature range of 450-980 °C and residence times of seconds for liquids and gases and longer for solids (HSDB 1996). Since benzene burns with a very smoky flame, dilution with alcohol or acetone is suggested to minimize smoke. Small quantities of benzene waste can be destroyed by chemical reaction. For example, treating benzene with dichromate in strong sulfuric acid for 1-2 days is sufficient for total destruction (HSDB 1996). Small quantities can also be ignited after pouring on dry sand or earth (OHM/TADS 1990).

Underground injection also appears to be an important disposal method in some states. Approximately 356,000 pounds of benzene (2.7% of the total environmental release) was disposed of by underground injection. This release via underground injection in 1992 was lower than the amount (654,000 pounds) released in 1992 (TRI90 1992). In addition, 340,000 pounds of benzene (2.6% of the total environmental release) was disposed of via land disposal (TRI92 1994). The amount discharged to soil in 1992 was less than half the amount (724,000 pounds) discharged in 1990 (TRI90 1992).

Several methods exist for the treatment of waste water that contains benzene: biological treatment (aeration or activated sludge process), solvent extraction, air and/or steam stripping, and activated carbon process (EPA 1994r; IRPTC 1985). Full-scale chemical treatability studies have demonstrated 95-100% reductions in benzene concentrations for industrial waste waters receiving biological treatments (HSDB 1996). A combination of steam stripping and air stripping, and a vapor extraction system that removes the separated benzene vapor may be suitable for the treatment of contaminated groundwater and soil (Naft 1992). An *in situ* bioremediation process has been used to decontaminate a site by delivering a controlled amount of nitrate (to accelerate biodegradation of benzene) to the site under hydraulic control (Kennedy and Hutchins 1992).